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## Review Article

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# 2. Novel truncated and stochastic approaches to configuration interaction

Jeremy P. Coe and Martin J. Paterson

*Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, UK*

**Abstract.** We review non-traditional approaches to configuration interaction including novel ways to truncate the configuration interaction wavefunction using perturbation, a priori selection and Monte Carlo procedures. Calculations of the full configuration interaction wavefunction using projector or diffusion Monte Carlo methods are also discussed. The authors' results using Monte Carlo configuration interaction for potential curves and non-variational quantities (multipole moments) are presented. The use of approximate natural orbitals to accelerate a Monte Carlo configuration interaction calculation is also investigated.

## Introduction

Full configuration interaction (FCI) offers the prospect of modelling a quantum system as accurately as possible within a given basis set, but the rapidly increasing number of states means that such calculations are computationally out of reach except for sufficiently small systems and basis sets. Traditional truncation methods, such as considering only single and double excitations with respect to a reference state, can reduce the calculation space but this may be at the expense of the accuracy and consistency of the correlation energy, and may neglect important configurations. However it is acknowledged that a large proportion of the states comprising a FCI wavefunction tend to have

Correspondence/Reprint request: Dr. Martin J. Paterson, Institute of Chemical Sciences, Heriot-Watt University Edinburgh, UK. E-mail: [m.j.paterson@hw.ac.uk](mailto:m.j.paterson@hw.ac.uk)

practically negligible coefficients. Here we review various non-standard approaches to configuration interaction (CI) that often stem from this observation to substantially reduce the size of the configuration interaction space while still aiming to capture the important aspects of the system.

## Background

Many-electron wavefunctions for  $N$  electrons can be constructed using Slater determinants (SDs) of  $N$  single-electron wavefunctions thereby ensuring that the total many-electron wavefunction is antisymmetric on exchange of particles. SDs are eigenfunctions of, say, the  $z$  component of the total spin operator with eigenvalue  $M_s = \frac{1}{2}(N_\alpha - N_\beta)$ .

$$\hat{S}_z \Psi = M_s \Psi \quad (1.1)$$

Here  $N_\alpha$  is the number of, say, spin up electrons, and  $N_\beta$  is the number of those of opposite spin. However SDs are not necessarily eigenfunctions of the total squared magnitude of the spin operator  $\hat{S}^2$ , defined by the eigenvalue equation, where  $S$  is the spin quantum number (equal to the maximum value of  $M_s$ ):

$$\hat{S}^2 \Psi = S(S+1) \Psi \quad (1.2)$$

Yet the exact eigenfunctions of the non-relativistic electronic Hamiltonian, which does not involve spin coordinates, are eigenfunctions of both these operators. To ensure that the approximate CI wavefunctions also satisfy this property then configuration state functions (CSFs) may be constructed using linear combinations of SDs.

The CI wavefunction is expressed as a linear combination of SDs or CSFs. This can be written as a reference configuration, often formed from the occupied Hartree-Fock (HF) orbitals in a given basis, then configurations formed by single substitutions (S) of an occupied HF molecular orbital with an unoccupied molecular orbital, then those formed by double substitutions (D) and so on,

$$\Psi_{CI} = c_0 \psi_0 + \sum_{\text{Singles}} c_i^S \psi_i^S + \sum_{\text{Doubles}} c_{ij}^D \psi_{ij}^D + \sum_{\text{N-folds}} c_{ijk\dots N}^N \psi_{ijk\dots N}^N + \dots \quad (1.3)$$

Or, in the notation of second quantization,

$$|\Psi_{CI}\rangle = c_0|\psi_0\rangle + \sum_{i,j} c_i^j \hat{a}_j^\dagger \hat{a}_i |\psi_0\rangle + \sum_{k<i, l<j} c_{ik}^{jl} \hat{a}_l^\dagger \hat{a}_k \hat{a}_j^\dagger \hat{a}_i |\psi_0\rangle + \dots \quad (1.4)$$

For a wavefunction comprising a linear combination of SDs or CSFs,

$$\Psi_{CI} = \sum_i c_i \psi_i \quad (1.5)$$

the coefficients and energy may be found by solving the eigenvector equation,

$$\mathbf{H}\vec{c} = \mathbf{E}\mathbf{S}\vec{c} \quad (1.6)$$

where

$$H_{ij} = \langle \psi_i | \hat{H} | \psi_j \rangle \quad (1.7)$$

$$S_{ij} = \langle \psi_i | \psi_j \rangle \quad (1.8)$$

For SDs the overlap matrix is the identity and the Hamiltonian matrix is constructed using the Slater-Condon rules. As the electronic Hamiltonian has at most two particle interactions then only entries where the configurations  $i$  and  $j$  differ by two or fewer orbitals are non-zero. This is true also for CSFs but the Hamiltonian and overlap matrix calculations are somewhat more complicated [1]. However the CI wavefunction formed from CSFs is an eigenfunction of the operator  $\hat{S}^2$  and the total number of states required is lower. For  $M$  basis functions,  $N$  electrons and total spin  $S$  it has been shown [2] that, when neglecting possible spatial symmetries, the total number of CSFs is,

$$N_{CSF} = \frac{2S+1}{M+1} \binom{M+1}{\frac{1}{2}N-S} \binom{M+1}{M-\frac{1}{2}N-S} \quad (1.9)$$

where binomial coefficients have been used, i.e.,

$$\binom{N}{r} = \frac{N!}{r!(N-r)!} \quad (1.10)$$

Using  $M_s = \frac{1}{2}(N_\alpha - N_\beta)$  the number of different SDs is,

$$N_{SD} = \binom{M}{\frac{1}{2}N + M_s} \binom{M}{\frac{1}{2}N - M_s} \quad (1.11)$$

For  $S=0$  then  $M_s=0$  and we have,

$$\lim_{M \rightarrow \infty} \frac{N_{SD}}{N_{CSF}} = 1 + \frac{1}{2}N \quad (1.12)$$

while the ratio is smaller for finite  $M$ , e.g.,  $M=16$ ,  $N=8$  gives approximately 3.8.

If all possible substitutions in the reference state are considered then this is known as a full CI (FCI) and the correlation energy is then defined as the difference between this energy and that of the HF energy. A traditional truncation of the FCI wavefunction is to only consider up to, say, double substitutions (CISD) or to limit substitutions to a predefined space. Such procedures can produce a computationally tractable calculation, but may severely affect accuracy by neglecting important configurations.

The contributions to the correlation are often roughly divided into static and dynamic where the former can be associated with the occurrence of a few large coefficients in the FCI expansion (a multi-configurational system). While dynamic correlation may be thought of as the remaining correlation energy. This can be associated with many small coefficients in the FCI.

If there is one dominant coefficient in the FCI wavefunction then the system would be expected to be well modelled using single-reference methods. Those based on the elegant and powerful method of coupled cluster (CC) [3,4], such as CCSD [5] and CCSD(T) [6] offer some of the best balances between accuracy and computational cost when the correlation is essentially classified as dynamic. Truncated coupled cluster in its usual incarnation is not variational, but is size extensive. A rough argument for part of the success of coupled cluster is that the employed exponential ansatz,

$$\Psi = e^{\hat{T}} \Psi_0 \quad (1.13)$$

means that a truncation of the excitation operator,

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots \quad (1.14)$$

to singles,

$$\hat{T}_1 = \sum_{ij} t_i^j \hat{a}_j^\dagger \hat{a}_i \quad (1.15)$$

and doubles, say,

$$\hat{T}_2 = \sum_{k<i, l<j} t_{ik}^{jl} \hat{a}_l^\dagger \hat{a}_k^\dagger \hat{a}_j \hat{a}_i \quad (1.16)$$

still includes higher excited determinants (e.g. part of the quadruples) in the coupled cluster wavefunction ,

$$e^{\hat{T}_1 + \hat{T}_2} = \left( 1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2!} \hat{T}_1^2 + \frac{1}{2!} \hat{T}_2^2 + \hat{T}_1 \hat{T}_2 + \dots \right) \quad (1.17)$$

The cluster coefficients in CCSD may be found efficiently using an iterative method: the scaling of a CCSD calculation with basis size (M) is  $O(M^6)$ , which is considered the typical scaling for CISD. The overall coefficient of a quadruple excited determinant, for example, in CCSD may not be the same as its counterpart in FCI, as some of the corresponding cluster coefficients (t) from higher excitation operators have not been included, but many of the neglected parts may be small enough so that the method works very well.

However if the system is multi-configurational then processes such as dissociation may not be modelled satisfactorily by techniques based on a single-reference. In these cases CCSD and CCSD(T) may perform poorly and multi-reference coupled cluster methods are currently not as well developed.

This static correlation may be accounted for using multiconfiguration self-consistent field (MCSCF) methods, see [7] and references therein. This is the multi-reference equivalent of Hartree-Fock where now the molecular orbitals and the configuration coefficients are optimised in a collection of SDs or CSFs. This shares the rapid escalation towards computational intractability with CI as the size of the basis and number of configurations becomes large. A feasible number of configurations must therefore be stipulated, but one is unlikely to know which are the important configurations to include and a search through configurations may be computationally inefficient.

In complete active space SCF (CASSCF) [8], all configurations involving substitutions within a subset of the MOs (the active space) are considered for a CI calculation and an MCSCF is implemented. This transfers the problem of configuration choice to that of orbital choice for the active space. With sufficient insight the important orbitals can be selected to

give good results and the use of the restricted active space method (RAS) [9] enables larger systems to be considered. Here the active space is subdivided into three where the number of occupied orbitals has a stipulated minimum in one space, a stipulated maximum in another and is unrestricted in the remaining space. These powerful methods will still eventually succumb to the factorial scaling of FCI and the approach is far from being ‘black box’: if the required insight is not forthcoming from the user, or the system is not readily amenable to this deduction, then the results may not be accurate enough. The use of approximate natural orbitals from a truncated CI calculation, which we will discuss later in this review, might be a way to give an estimate of the important orbitals with minimal user input. Assuming that the important orbitals have been chosen then the neglected dynamic part of the correlation may be partly recovered if necessary by using, for example, perturbation such as CASPT2 [10], or further CI on top of the optimised reference configurations leading to several variants of multi-reference CI (MRCI). MRCI has some advantages over multi-configurational perturbational schemes as analytical derivatives with respect to nuclear motion, and non-adiabatic couplings, are somewhat easier to implement.

CI can, in principle, deal with both static and dynamic correlation and the benefit of such an approach is that it is relatively straightforward to implement, gives the most accurate energy within a given basis for a FCI, and is variational although not usually size extensive. The clear difficulty is that a FCI, and even a standard truncation that leaves many substitution levels, is only computationally accessible for small systems and basis sets due to the rapid increase in the number of configurations as the number of basis functions increase. However many configurations may have practically negligible coefficients in a FCI and therefore may be neglected in the calculation. If such configurations were known beforehand then the calculation could be made smaller, perhaps small enough to be computationally tractable and still able to capture the essential qualities of the system.

Novel methods of truncating the CI wavefunction by a priori estimation of the important configurations, perturbative approaches or stochastic procedures have therefore been proposed. In addition diffusion or projector Monte Carlo methods of approaching the FCI coefficients have been shown to be successful as an alternative to the direct diagonalization of the eigenvector equation. We explore some of these recent developments in this review.

## A priori estimates

In [11] L. Bytautas and K. Ruedenberg estimate the importance of more substituted configurations (e.g. quadruples) by using the coefficients from a

truncated calculation considering up to triple substitutions (CISDT). They define the weight of a given choice of spatial orbitals as,

$$C_{SP} = \sum_K^{N_{SP}} c_K^2 \quad (1.18)$$

This uses the coefficients of all configurations consisting only of the required spatial orbitals and the configurations therefore differ only by the spin part of the orbitals. For example,  $C_{ab}^{ij}$  is the weight of all configurations where orbitals a and b in the reference are replaced by orbital i and j. A higher order weight is then estimated using the product of double and triple substituted configurations which produce it, e.g.,

$$C_{abcd}^{ijkl} = \sum C_{ab}^{ij} C_{cd}^{kl} \quad (1.19)$$

Here all distinct ways to make the quadruple substituted configuration from two double substitutions are summed over. The total estimated weight for the quadruples is then converged upon by increasing the number of double or triple substitutions considered. For NCCN with a cc-pVTZ basis they find that truncation after a CISDTQ calculation and their a priori truncation show close agreement. There they report that 60,245 configurations give 0.71 mHartree error compared with the full CISDTQ space of 776,316 determinants. For N<sub>2</sub> and HNO they also find that the results of post and prior truncation produce similar results.

M. C. Troparevsky and A. Franceschetti put forward a method to a priori identify relevant configurations for electronic states in nanostructures [12]. This is termed optimized configuration interaction (OCI) whereby simulated annealing is used to optimise a small set of configurations. Here the Hamiltonian matrix is constructed and the energy found by diagonalization then a trial move consisting of a single substitution in one SD is made. The Hamiltonian matrix is again computed and diagonalized. This trial move is then either rejected or accepted with probability,

$$P = e^{-\Delta E / k_B T} \quad (1.20)$$

Another trial move is then considered and the process continues. Here  $\Delta E$  is the change in energy of the state of interest and  $k_B$  is the Boltzmann constant. The simulated annealing temperature  $T$  is initially set so around 50% of the moves are not rejected, and then gently reduced to result in a stable final state. Interestingly they find that for  $K$  configurations the OCI



configurations are not necessarily the same as the  $K$  configurations with the largest coefficients in an FCI. They note that the energy converges faster towards that of the FCI in OCI compared with CI as the number of configurations increase. However the circa ten thousand steps of the simulated annealing algorithm results in overall similar computational expense to CI. Their results suggest, though, that the OCI for  $N+1$  configurations contains the OCI for  $N$  configurations thereby possibly allowing a more efficient use of the algorithm in comparison with standard truncated CI.

## Estimates from perturbation theory

In [13] R. J. Harrison uses second-order perturbation theory to increase the CI space in a controlled manner (CI+PT) and approach the FCI energy. A CI calculation is performed in a reference space then, for the  $K$ 'th eigenvector of interest, each configuration  $|I\rangle$  that interacts with, but does not feature in, the current space is considered to compute an energy lowering,

$$\Delta E_K = \sum_I \frac{|\langle I | \hat{H} | K \rangle|^2}{E_K - \langle I | \hat{H} | I \rangle} \quad (1.21)$$

If the contribution from any  $|I\rangle$  is greater than a threshold, then  $|I\rangle$  is included in the reference space for the next iteration. The process is repeated until no new configurations are added for a given threshold. It is noted that the final result of a truncated CI space plus the perturbation is within 0.1 kcal/mol of the FCI result for the systems they consider. The size of the space is also much smaller than the FCI. For example, the oxygen anion with a FCI comprising 648,062 CSFs only required 3.2% of these in the truncated space and 67% in the final perturbation calculation. For calculations in larger spaces, they find that an even smaller fraction of the space is required: their method, at the smallest threshold they consider, uses only 0.002% of the FCI space for the reduced CI space and 0.8% in the perturbation correction for the magnesium atom with a FCI space of 504,565,691 CSFs. A. L. Wulfov implements a CI-PT procedure for desktop computers [14] and finds that the CI+PT results are within 0.3 kcal/mol of the known FCI results for the  $\text{NH}_2$  radical. The procedure is tested on a very large space for the HF dimer ( $\sim 3 \times 10^{14}$ ) and, for large inter-molecular distance, the results are not in disagreement with the expected value using twice the FCI result for the single molecule. A basis for the HF dimer (4s3p1d/2s1p) is also considered where the full space would require around  $4 \times 10^{15}$  states for which the CI+PT calculation time was a day.

## DMRG calculation of reduced CI space

In [15] K. Boguslawski, K. H. Marti and M. Reiher construct a CI wavefunction from the results of using small density matrix renormalization group (DMRG) calculations. They note that as the numerical DMRG does not require an analytic CI expansion beforehand then such a procedure, with a small number of states, could be used to quickly find possible important configurations for use in further multi-reference CI calculations. For ozone with a FCI reference space of 7,956 their results with a coefficient threshold of 0.0001 give 1,532 determinants and a deviation of 3.6 kJ/mol from the FCI reference space energy. The accuracy may be improved by reducing the threshold for the CI coefficients and/or increasing the size of the space for the DMRG calculation. A system and basis which is beyond carrying out a CI in the full reference space is then considered, 1,3-dimethyl Arduengo carbene. Their procedure requires only 70,916 of the  $8 \times 10^{12}$  CI states to capture 99.998% of the DMRG energy.

## FCI quantum Monte Carlo

While the aforementioned work tended to consider a reduction in the FCI space then direct solution of the eigenvector equation, interesting work has also been done in using the full FCI space but finding the energy and coefficients using Monte Carlo procedures. The idea is based on the diffusion Monte Carlo method (DMC) which can tend towards the exact wavefunction. However this will be the bosonic not fermionic ground state unless the nodes are stipulated. Unfortunately the exact nodes are unknown without the exact wavefunction (the sign problem). Y. Ohtsuka and S. Nagase put forward an algorithm to carry out diffusion or projector Monte Carlo on a space of CSFs in [16] (PMC-CSF), and G. H. Booth, A. J. W. Thom and A. Alavi in [17] develop an algorithm (FCIQMC) for Slater determinants. In these methods nodes do not need to be defined, but this comes at the expense of the size of the calculation: the Monte Carlo simulation is now dependent on the basis and scales as the FCI space. However it may still be more efficient with regards to time and memory than traditional diagonalization for a FCI calculation: the following results show that the number of walkers can be significantly smaller than the FCI space and the algorithm has good prospects for large parallel calculations. The methods are based on the imaginary time Schrödinger equation,

$$\frac{\partial \Psi}{\partial \tau} = -\hat{H}\Psi \quad (1.22)$$

whose solution can be written,

$$\Psi(\tau + \Delta\tau) = e^{-\Delta\tau\hat{H}}\Psi(\tau) \quad (1.23)$$

The expansion of an initial wavefunction in eigenstates of the system suggests that as the ground state has the lowest energy its term will become the largest in the long time limit. Here the Hamiltonian is perhaps shifted by a constant energy. Hence the ground state will be projected out if it has non-zero overlap with the initial trial function.

In [17] G. H. Booth, A. J. W. Thom and A. Alavi define the operator,

$$\hat{K} = \hat{H} - E_{HF} \quad (1.24)$$

to replace the Hamiltonian. The expansion of a wavefunction in Slater determinants,

$$\Psi(\tau) = \sum_j C_j(\tau) |D_j\rangle \quad (1.25)$$

is then substituted into Eq. (1.22). Acting on this from the left with  $\langle D_i |$  and introducing an energy shift  $S$ , used to control the walker population, leads to,

$$\frac{\partial C_i}{\partial \tau} = \sum_j (K_{ij} - S\delta_{ij}) C_j \quad (1.26)$$

This is modelled using a population dynamics algorithm with  $N$  walkers each carrying a sign of positive or negative 1 and associated with a determinant  $i$ . The sum of the signs of the walkers on a determinant is used to approximate the coefficient  $C_i$  for that determinant. There are three steps to this algorithm beginning with a set of walkers, denoted as the parents, and using a time step  $\delta\tau$ .

All parent walkers are considered for the first two steps. The first step is defined by G. H. Booth, A. J. W. Thom and A. Alavi as the spawning step. Here a determinant  $j$  differing by at most a double substitution from the current determinant  $i$  is chosen with probability  $p_{\text{gen}}$ , another walker is then created there with probability,

$$p_s = \frac{\delta\tau |K_{ij}|}{p_{\text{gen}}} \quad (1.27)$$

If  $p_s$  is greater than 1 then the number of walkers created is at least the integer part of  $p_s$  with the remaining fraction defining the probability of a walker being created in addition to this. The sign of the new walkers are the same as the parent unless  $K_{ij} > 0$  in which case the sign is reversed. The death/cloning step then calculates,

$$p_d = \delta\tau(K_{ii} - S) \quad (1.28)$$

and if  $p_d > 0$  the walker is removed with this probability. Otherwise a copy of the walker is made with probability  $|p_d|$ . When these two steps have been carried out for the parent walkers an annihilation step is used on all walkers. Here pairs of walkers with opposite sign residing on the same determinant are removed. The three steps are then repeated.  $S$  is chosen to initially allow a large enough number of walkers then adjusted to keep the population controlled at roughly constant  $N$ . The time evolution equation for the coefficients reveals that  $S$  should become equal to the correlation energy when a steady state is reached.

This algorithm is used for a range of atoms and molecules in [17]: Ne with a aug-cc-pVDZ basis and  $C_2$ ,  $H_2O$  and  $N_2$  with cc-pVDZ. The size of the FCI space ranges from  $\sim 6 \times 10^6$  to  $\sim 5 \times 10^8$ , and results of essentially FCI accuracy are found for the algorithm where the ratio of walkers to the FCI space varies from 0.031 to 0.637.

Using the PMC-CSF method, the dissociation of LiH in the 6-31++G(d,p) basis was considered in [16] by Y. Ohtsuka and S. Nagase. This work found that the maximum deviation in the potential curve for  $1 \times 10^5$  walkers was 0.87 mHartree when compared with an FCI of 9,415 states.

In [18] Y. Ohtsuka and S. Nagase find the first ten energy states of water in the STO-3G basis (133 states in the FCI) with accuracies close to that of FCI using  $5 \times 10^4$  walkers. For LiF with a FCI space of around  $7.7 \times 10^7$ , the maximum deviation of the QMC energy from the FCI energy was 2 mHartree with  $5 \times 10^6$  walkers, for both the ground and first excited state. The avoided crossing in the potential curves was located around the same point as for the FCI. For LiF the time required for PMC-CSF was less than a quarter of that needed for a FCI and the FCI needed more than 14 times the amount of memory.

G. H. Booth and A. Alavi use the FCIQMC method in [19] on atoms and cations from atomic number  $Z=3$  to  $Z=12$ . The aug-cc-pVXZ basis is increased from double zeta to quadruple zeta for all except magnesium (due to CPU time constraints) and to quintuple zeta, where it was available, for  $Z < 10$ . The ionization energies are found to be within 2 mHartree of the exact

non-relativistic ionization energies for the largest basis set considered, except for sodium, neon and magnesium whose results fall a little outside chemical accuracy. Here sodium had the largest difference of around 4.3 mHartree. For the largest basis set considered, the calculation for oxygen, fluorine and neon was truncated to include only up to six substitutions in the reference. The ratio of number of walkers to the FCI space varied, but was always very small. The largest ratio values were for the neon atom at around 0.0014 and for the cation at about 0.0002. For aug-cc-pVQZ, the FCI space is around  $10^{15}$  SDs for the sodium atom but it only required around 2,000 walkers, while 100 million were needed for the oxygen atom.

Electron affinities are considered by D. M. Cleland, G. H. Booth and A. Alavi in [20] using FCIQMC, and also a modification, the i-FCIQMC method. In i-FCIQMC the reference determinant and those with a walker population greater than a threshold are deemed initiator determinants and permitted, in theory, to create other walkers on any coupled determinant. Walkers residing on other determinants can only create new walkers if the coupled determinant is already occupied by at least one walker of the same sign. This method gave almost equivalent results to FCIQMC for electron affinities while offering a reduction in the number of walkers. For the elements considered results were within 2 mHartree of the exact non-relativistic affinities for the largest aug-cc-pVXZ basis considered ( $X=4$  or  $5$ ). For example, one of the largest FCI spaces (around  $10^{16}$ ) was for the fluorine anion but this only required  $10^7$  walkers for the i-FCIQMC.

The potential curves of the carbon dimer are investigated using FCIQMC by G. H. Booth, D. Cleland, A. J. W. Thom and A. Alavi in [21]. For a 6-31G\* basis the FCIQMC and i-FCIQMC methods were compared with the FCI results of M. L. Abrams and C. D. Sherrill [22] and found to be essentially of FCI accuracy (mean deviations of -0.013 and -0.017 mEh respectively). The FCI space was around  $5 \times 10^7$  determinants while the i-FCIQM needed around  $2 \times 10^6$  walkers. Bases up to cc-pVTZ were then considered. Two of the considered low-lying states of  $C_2$   $^1\Sigma_g^+$  and  $^1\Delta_g$  have the same spatial symmetry within  $D_{2h}$ . Therefore they differentiated between them by transforming the orbitals to eigenfunctions of the  $\hat{L}_z$  operator and requiring conservation of  $M_L$  in the determinant space. Time reversal symmetry, whereby the coefficient for a determinant is  $(-1)^S$  that of the determinant with spins swapped over, was also used to halve the size of the required space. For cc-pVTZ they found only  $2 \times 10^6$  walkers were necessary to see convergence of the i-FCIQMC energy (to around 0.1 mHartrees) to the extrapolation by intrinsic scaling result of L. Bytautas and K. Ruedenberg

[23]. The size of the full symmetry allowed space was around  $5 \times 10^9$  and hence precludes a comparative standard FCI calculation.

## Monte Carlo configuration interaction

We finally consider the Monte Carlo configuration interaction (MCCI) method of J. C. Greer [24]. This is an iterative procedure that randomly augments a truncated CI approximation to the wavefunction with coupled states, then diagonalizes the system and removes those states with coefficients less than a threshold ( $c_{\min}$ ). This process is continued until the energy has converged. Thereby enabling a compact approximation to the FCI wavefunction to be produced that can still perhaps account for a large amount of the correlation energy even in multi-configurational situations and without prior knowledge of the important states. CSFs are used in the parallel MCCI program developed by L. Tong, M. Nolan, T. Cheng and J. C. Greer [25] so ensuring that the MCCI wavefunction is an exact spin eigenfunction.

The dissociation of HF and of water is considered by J. C. Greer using MCCI in [26]. For HF with a DZ basis the CISD results diverge as the bond length is increased compared with the FCI, but MCCI with  $c_{\min}=10^{-3}$  follows the FCI results with errors of only a few meV. As the OH bond length is increased for water in a DZP basis, MCCI with  $c_{\min}=10^{-3}$  has a roughly constant error of around 0.01 Hartrees compared with the FCI results. In this case CISD again diverges, although CISD with the Davidson correction is more accurate at a bond length of 1.5 times that at equilibrium.

Electronic excitation energies for a selection of first-row atoms and silicon are calculated using MCCI by J. A. Larsson, L. Tong, T. Cheng, M. Nolan and J. C. Greer in [27]. Average errors of less than 100meV compared with experimental results were achieved with  $c_{\min}=10^{-3}$  and the aug-cc-pVTZ+R(s,p) basis. The MCCI work on electronic excitations is extended in [28] where W. Györrfy, R. J. Bartlett and J. C. Greer investigate the electronic spectra of small molecules. They note that the number of CSFs required varied from a few thousand to around twelve thousand for  $c_{\min}=5 \times 10^{-4}$  while the FCI spaces tended to be of the order of  $10^8$ . For  $H_2O$  with an aug-cc-pVDZ basis and including diffuse functions, the results for the first eleven states had maximum error of 0.093eV. Even the difficult multi-reference  $C_2$  had an error always lower than 0.177 eV in the excitation energies of the first eleven states and lower than 0.0048 eV if the two most problematic states were excluded. Interestingly, their MCCI results enabled them to spot a mistake in the labelling of a state in previous FCI results for one of the difficult  $C_2$  states ( $^3\Delta_g$ ). For  $CH_2$  in a aug-cc-pVDZ basis the

MCCI results were within 0.073 eV of the FCI excitation energy for the nine states considered.

A procedure that shares some aspects with that of MCCI is put forward in [29]. Here M. Sambatoro, D. Gambarcorta and L. Lo Monaco consider a small CI expansion and carry out a sequence of diagonalizations to determine if the energy is lowered by more than a defined amount by the addition of a double or single substitution. If so then the CI expansion is updated. When all the single and double substitutions for the components of the original expansion have been considered then the final energy is compared with the initial. If sufficiently similar then the procedure terminates, otherwise the new CI expansion, with a coefficient threshold determining the inclusion of states, is used for another series of diagonalizations. They model the eight valence electrons in an  $\text{Na}_8$  cluster and find that their procedure, with thresholds for energy and coefficients both set at zero, essentially recreate the FCI results when the space is restricted to SDs formed from the five lowest HF orbitals. For a larger space of  $1.7 \times 10^8$  SDs and coefficient threshold  $10^{-3}$  they find that the correlation energy from their method is about 2% lower than a traditionally truncated CI calculation.

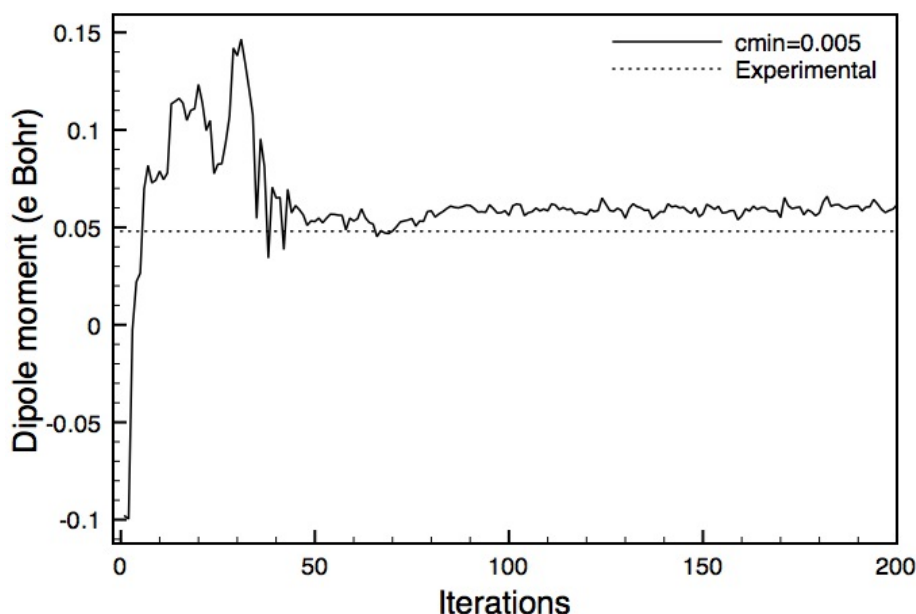
## Authors' results

We have applied the MCCI program to non-variational quantities such as the dipole moment of carbon monoxide. For a linear molecule orientated along the  $z$  axis then the dipole moment, when using atomic units, may be calculated as,

$$\mu = -\langle \Psi | \hat{z} | \Psi \rangle + \sum_i z_i Q_i \quad (1.29)$$

where  $Q_i$  is the charge of nucleus  $i$ . The dipole moment of carbon monoxide, although small, when calculated with Hartree-Fock (HF) strikingly has the incorrect sign compared with experimental results. Previous work has suggested that this dipole calculation is sensitive to the amount of correlation recovered [30]. The bond length of 2.1316 Bohr and experimental dipole value is taken from [30].

With a cc-pVDZ basis, two frozen core orbitals and a relatively large  $c_{\min}=5 \times 10^{-3}$ , we see in figure 1 that the MCCI method, starting from the incorrectly signed result of the HF single SD, quickly reaches a value only a little above that of experiment. The non-variational nature is apparent in the plot. This value used only 833 CSFs compared with a FCI of around  $4 \times 10^9$  SDs.



**Figure 1.** MCCI dipole moment calculation for CO in a cc-pVDZ basis with two frozen core orbitals.

To get to 98% of the correlation energy,  $c_{\min}=3 \times 10^{-4}$  and 40,000 CSFs were needed though. Interestingly, at this value of  $c_{\min}$  the match with the experimental dipole result is worse (Fig. 2). Here the results from a previous calculation with larger  $c_{\min}$  have been used as the initial wavefunction and the procedure restarted. These results suggest that even the FCI for this basis would perhaps not give an accurate dipole.

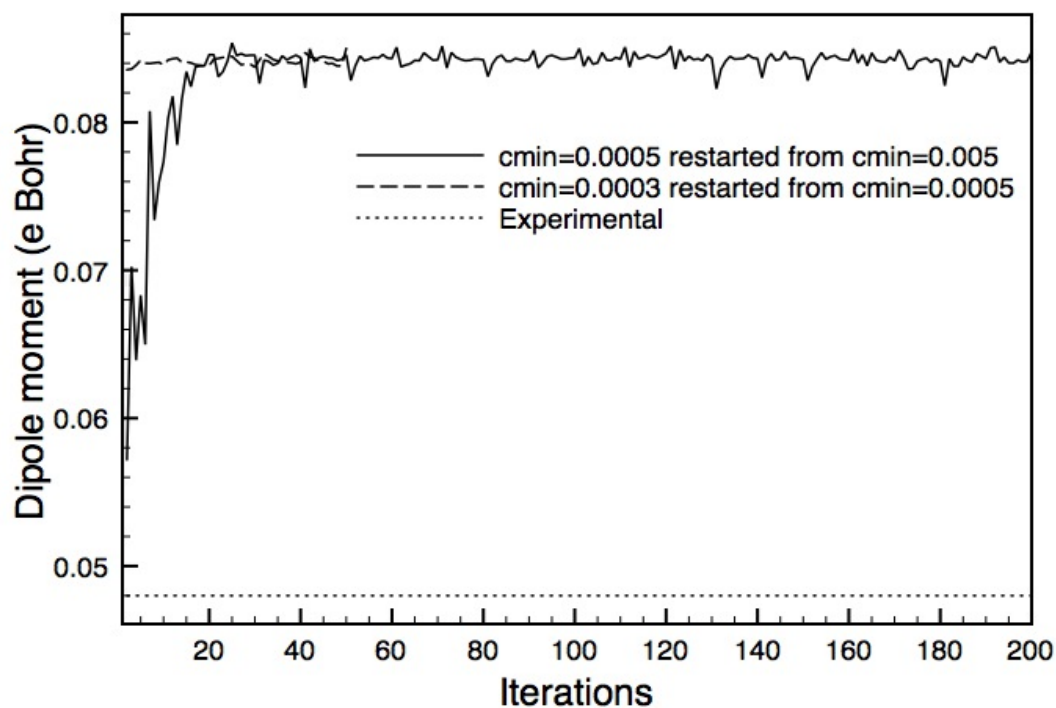
However as diffuse basis function would be expected to be important for the calculation of multipoles, we also considered the aug-cc-pVDZ basis with no frozen core orbitals (Fig. 3). Here we found that a very good agreement with experiment was recovered as we reduced  $c_{\min}$  to  $3 \times 10^{-4}$ . This used around 60,000 CSFs compared with the FCI space of around  $10^{15}$  SDs.

We now consider the quadrupole moment of  $N_2$  using an aug-cc-pVDZ basis with bond length  $R=2.07432$  bohr and all electrons correlated. The molecule is oriented along the z-axis with the centre of mass at the origin. The traceless quadrupole tensor is then calculated using the definition of Buckingham [31]. For a linear molecule oriented along the z axis we calculate the zz component of the traceless quadrupole tensor as,

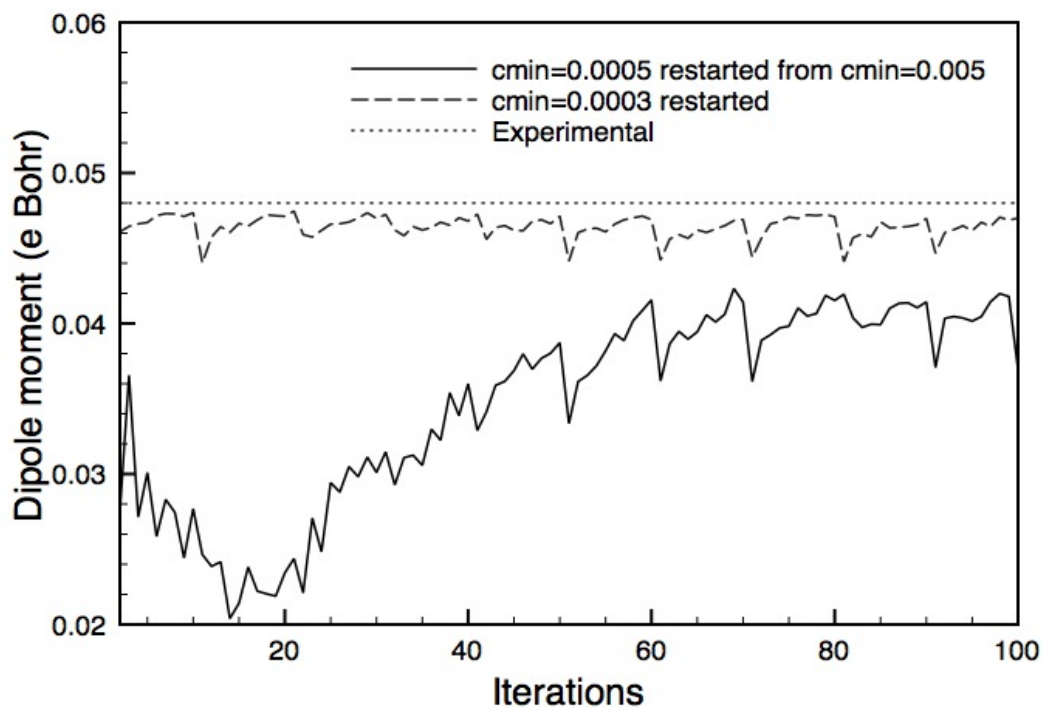
$$\Theta_{zz} = -\langle \Psi | \hat{z}^2 | \Psi \rangle + \frac{1}{2} \langle \Psi | \hat{x}^2 | \Psi \rangle + \frac{1}{2} \langle \Psi | \hat{y}^2 | \Psi \rangle + \sum_i z_i^2 Q_i \quad (1.30)$$

which is displayed in Fig. 4. Here we again see that the MCCI results quickly reach a value within the experimental bounds and the non-variational nature

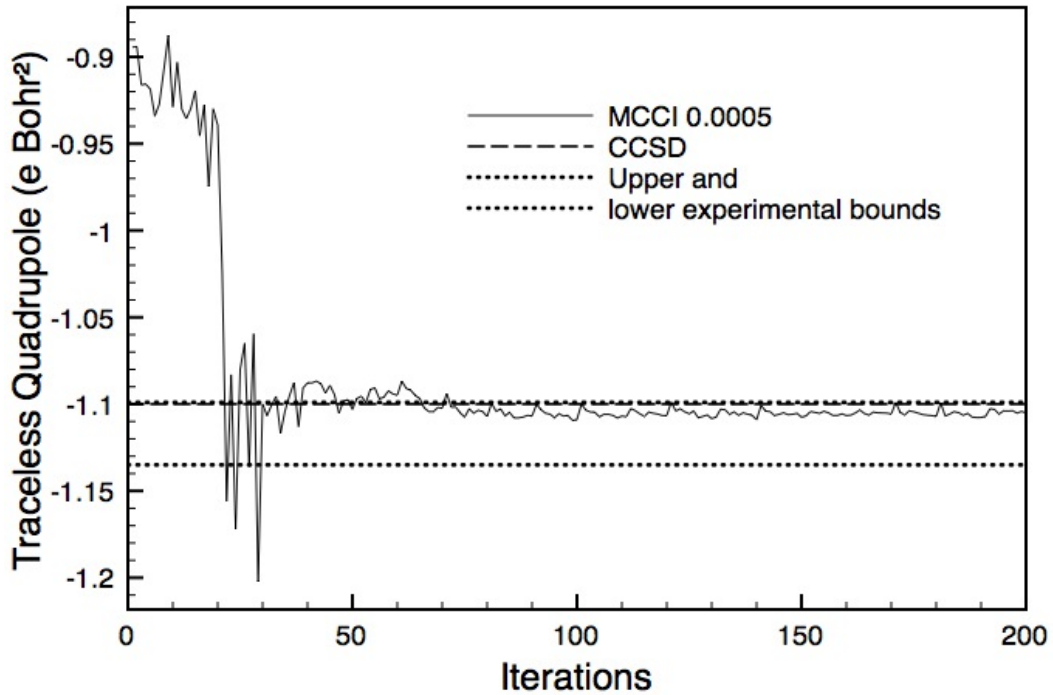




**Figure 2.** Smaller  $c_{\min}$  MCCI calculation of the dipole moment of CO in a cc-pVDZ basis with two frozen core orbitals.



**Figure 3.** Aug-cc-pVDZ basis MCCI calculation of the dipole moment of CO.



**Figure 4.** The  $zz$  component of the traceless quadrupole tensor of  $N_2$ . Computational results used an aug-cc-pVDZ basis. Experimental results are from [32].

is evident. The CCSD result is fairly similar to that of MCCI which might be expected as although CCSD has difficulties with the dissociation of  $N_2$ , due to its multiconfigurational nature, this multipole result is at the equilibrium geometry. The MCCI result required 21,686 CSFs while the FCI space, without symmetry considerations, is around  $2 \times 10^{15}$  SDs.

We have also used a modified version of the MCCI algorithm to calculate the potential curve for the  $C_2$  molecule in a 6-31G\* basis when using two frozen core orbitals. This system and basis appear challenging as FCIQMC required over a million walkers [21].

With a coefficient threshold of  $c_{\min} = 5 \times 10^{-4}$  MCCI required 6,900 CSFs on average for the carbon dimer potential curve while the FCI calculation used circa  $5 \times 10^7$  SDs [22]. As a potential is defined only up to an additive constant then the non-parallelity error (NPE) [33] may be considered a good choice to quantify the match between two potential curves:

$$NPE = \max_R |E_R^{FCI} - E_R^{approx}| - \min_R |E_R^{FCI} - E_R^{approx}| \quad (1.31)$$

This would be zero if two curves differ by a constant energy shift.

We compare the MCCI results to those of single reference methods reported in [22] in table 1. The accuracy of the potential as quantified by the

**Table 1.** NPE values for the carbon dimer in a 6-31G\* basis. Single-reference results from [22].

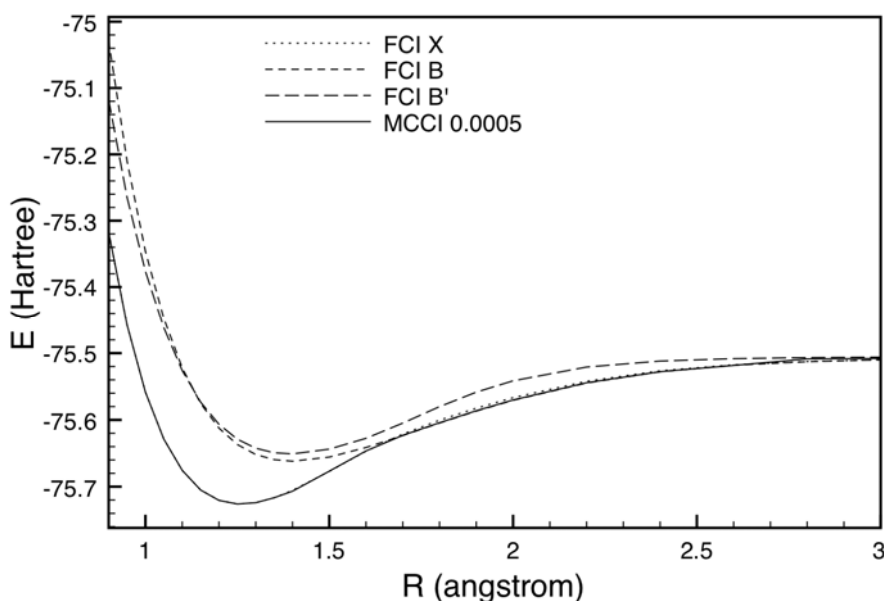
Method	NPE (kcal/mol)
MCCI 0.0005	4.8
CCSD	24.3
CCSD(T)	61.3
UCCSD	27.0
UCCSD(T)	21.6
CISDTQ	16.6

NPE can be seen to be very good for MCCI and better than all the considered single-reference methods. Given that even a CISDTQ calculation would be expected to require a few million SDs, the accuracy of the MCCI result with only around 6,900 CSFs demonstrates the usefulness of non-standard truncations.

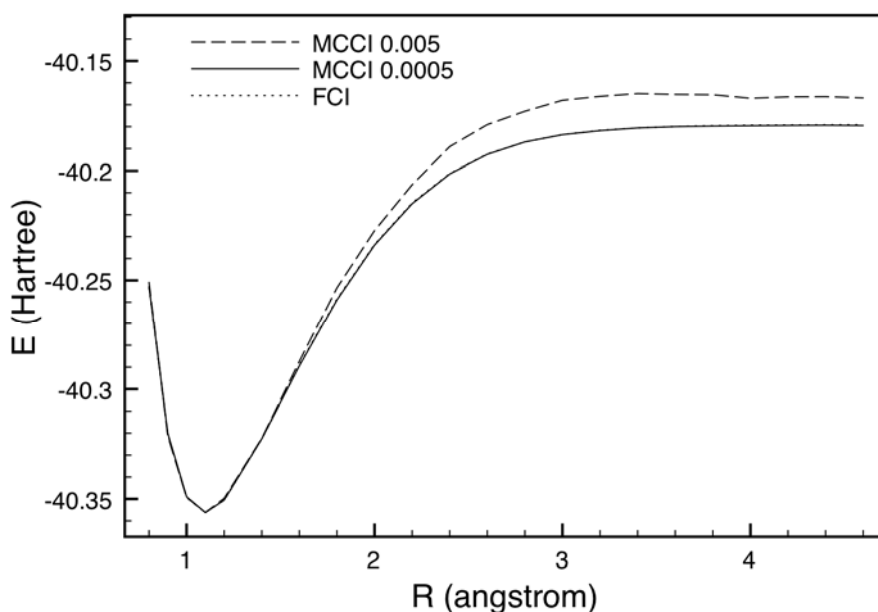
The potential curve is of slightly higher accuracy, in a sense, than its constituent single-point energy calculations: the mean single-point error was around 6.0 kcal/mol. In Figure 5 we display the MCCI potential curve shifted by a constant so that it coincides with the FCI ground state minimum. Here X and B' are  $^1\Sigma_g^+$ , while B is  $^1\Delta_g$ . The curve appears a very good fit except for bond lengths (R) close to 3 angstrom where it appears that a low lying excited state B' has been converged upon. In addition, the lowest energy state between about 1.7 and 2.5 angstroms is B rather than X and the MCCI seems to have converged to this as would be expected: the states are very close in energy and have the same spatial symmetry in the abelian subgroup used ( $D_{2h}$ ). If we exclude the two points around R=3 then the average single point energy error only reduces a little to 5.7 kcal/mol but the NPE is now only 2.7 kcal/mol.

We next compare the potential curve for hydrogen dissociation in CH<sub>4</sub> and BH using MCCI, with the results of FCI and single reference methods from [33]. For each system one frozen core orbital is utilised.

For CH<sub>4</sub> a tetrahedral geometry is used with a bond length of 1.086 angstroms for the three fixed C-H bonds. We see in Fig. 6 that with a 6-31G\* basis the MCCI curves are qualitatively correct even with  $c_{\min}$  as large as  $5 \times 10^{-3}$  as we vary the length (R) of one C-H bond. With the curves shifted so that their minima coincide the  $c_{\min}=5 \times 10^{-3}$  energy is too high at large R but the  $c_{\min}=5 \times 10^{-4}$  is indistinguishable from the FCI curve on this scale.



**Figure 5.** MCCI potential curve shifted in energy to coincide with the minimum of the FCI curve and compared with FCI results for the carbon dimer in a 6-31G\* basis.



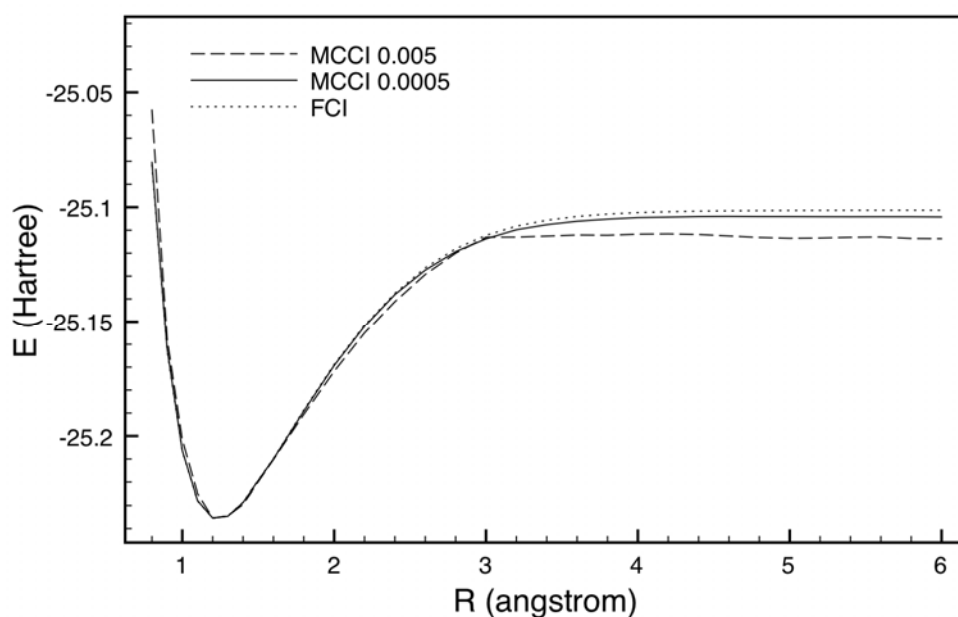
**Figure 6.** MCCI potential curve shifted in energy to coincide with the minimum of the FCI curve and compared with FCI results for methane in a 6-31G\* basis.

This accuracy of the MCCI curve for  $\text{CH}_4$  is quantified in table 2 where we see that its NPE is equivalent to that of CCSD when using  $c_{\min}=5 \times 10^{-3}$  and five times smaller than that of UCCSD(T) when using  $c_{\min}=5 \times 10^{-4}$ . We note that a FCI requires a space of 26,755,625 SDs [33] while the mean number of CSFs in the final MCCI wavefunction was 417 and 4272 for the larger and smaller  $c_{\min}$  respectively.

**Table 2.** NPE values for hydrogen dissociation. Single-reference results from [33].

Method	CH <sub>4</sub> NPE (kcal/mol)	BH NPE (kcal/mol)
MCCI 0.005	10.3	22.8
MCCI 0.0005	0.6	2.6
CCSD	10.3	8.1
CCSD(T)	-	23.3
UCCSD	5.1	4.7
UCCSD(T)	3.2	3.1

For BH an aug-cc-pVQZ basis was used and the mean number of CSFs for MCCI with  $c_{\min}=5\times 10^{-3}$  was 333 while 4220 were found when  $c_{\min}=5\times 10^{-4}$ , again this is in sharp contrast to the FCI space of 15,132,412 [33]. Fig. 7 shows that MCCI again captures the qualitative behaviour of the FCI potential energy curve however now when  $c_{\min}=5\times 10^{-3}$  the shifted potential is too low at large  $R$  and for the smaller  $c_{\min}$  results it can be seen that there is a slight difference in the curves with the shifted MCCI being a little too high at large  $R$ . The NPE results in table 2 reveal that MCCI with  $c_{\min}=5\times 10^{-3}$  is now substantially higher than CCSD but, interestingly, a little lower than CCSD(T). While when  $c_{\min}=5\times 10^{-4}$  the MCCI results have a lower NPE than all the considered single-reference based methods but, with the somewhat larger MCCI NPE of 2.6 kcal/mol, the difference is not as marked as with methane.

**Figure 7.** MCCI potential curve shifted in energy to coincide with the minimum of the FCI curve and compared with FCI results for BH in an aug-cc-pVQZ basis.

We also consider the use of approximate natural orbitals (NOs) to improve convergence in MCCI. The Hartree-Fock molecular orbitals (MOs) give the lowest energy single Slater determinant wavefunction, but they may not offer optimum convergence for a truncated CI calculation. The NOs are eigenvectors of the first-order reduced density matrix or one-matrix [34],

$$\gamma(\vec{x}_A, \vec{x}_B) = N \int \Psi^*(\vec{x}_A, \vec{x}_2, \dots, \vec{x}_N) \Psi(\vec{x}_B, \vec{x}_2, \dots, \vec{x}_N) d\vec{x}_2 \dots d\vec{x}_N \quad (1.32)$$

$$\gamma(\vec{x}_A, \vec{x}_B) = \sum_{i=1}^M \sum_{j=1}^N \phi_i^*(\vec{x}_A) \gamma_{ij} \phi_j(\vec{x}_B) \quad (1.33)$$

and are considered to give better convergence than the canonical HF MOs. One aspect of their functionality is that some NOs may have negligible eigenvalues so may be discarded resulting a smaller basis. For a system of two electrons it was demonstrated that NOs are indeed optimal [35]. For more electrons, interestingly [11] uses split-localised FORS molecular orbitals which are stated to possibly result in better convergence than NOs for larger systems.

The exact one matrix for a given basis is unfortunately unknown without carrying out a FCI so we approximate the one matrix using the MCCI wavefunction from a run of 50 iterations. We build up the one-matrix by noting that SDs  $i$  and  $j$  in maximum coincidence only contribute if they have no differences,

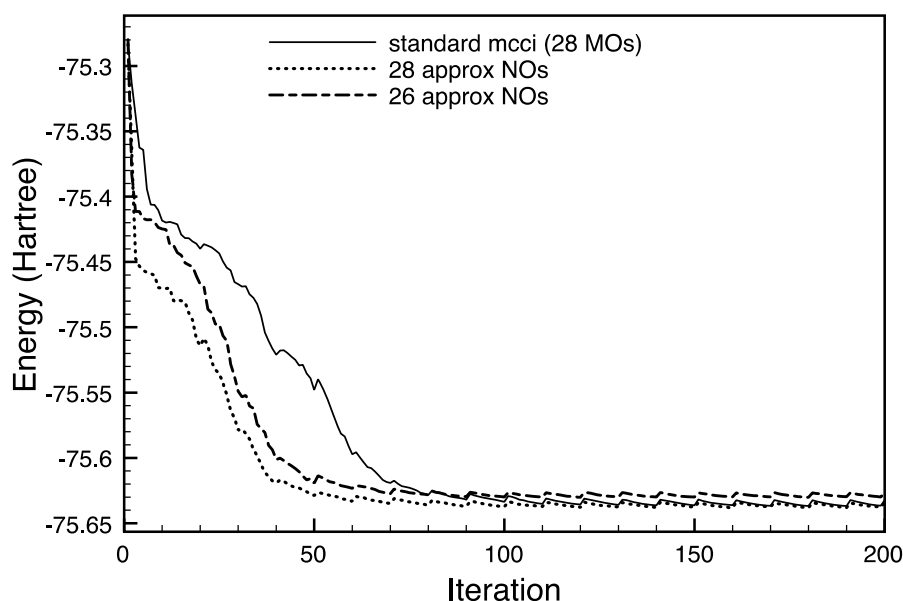
$$\gamma_{mm} \rightarrow \gamma_{mm} + e_p c_i^* c_j \quad (1.34)$$

where  $m$  runs over all occupied orbitals in the SD. Or one difference (orbitals  $k$  and  $l$ ),

$$\gamma_{kl} \rightarrow \gamma_{kl} + e_p c_i^* c_j \quad (1.35)$$

where  $e_p$  is the sign from permuting orbitals in the SDs so that the two SDs have maximum coincidence. We average over spins, diagonalize the one-matrix and then transform the molecular orbital (MO) integrals into NO integrals.

For the carbon dimer in a 6-31G\* basis, with an eigenvalue cut-off of  $10^{-5}$  we have 28 NOs while  $10^{-4}$  leaves us with 26 NOs. Figure 8 shows how the MCCI convergence per iteration is accelerated using natural orbitals and twelve processors.



**Figure 8.** MCCI convergence with natural and canonical Hartree-Fock orbitals for the carbon dimer with a bond length of 1.6 angstroms and a 6-31G\* basis.

The graph (Fig. 8) does not reveal the cost per iteration nor the overhead from calculating the natural orbitals. When these data are taken into account we find that the total time to  $E < -75.626$  Hartree using 26 NOs was 364 seconds while 28 NOs required 153 seconds, this compares with 233 seconds for standard MCCI. Hence overall it appears that certain approximate NO calculations can offer an overall reduction in time for an MCCI calculation and it would be hoped that this reduction could be more pronounced and important for larger systems.

The eigenfunctions of the second-order reduced density matrix could also be computed and used as an estimate of the natural geminals. Such an estimate could perhaps be useful in accelerating convergence when using explicitly correlated wavefunctions such as R12 methods [36]. The MCCI estimate of the natural orbitals could also maybe be used as a starting point for CAS and RASSCF calculations (see background section) to reduce the amount of insight required from the user when selecting the active space.

## Conclusions

The results discussed in this review show that many of the configurations in a full configuration interaction can indeed be neglected while still capturing much of the quality of the exact wavefunction. The featured novel perturbative, a priori, or stochastic approaches to configuration interaction essentially attempt to seek out the important configurations and at this they

appear to be successful: we have seen how they often allow very compact wavefunctions with sufficiently accurate energies to be found relatively efficiently and outperform traditional truncations of the configuration interaction wavefunction.

In a sense, coupled cluster began its life in nuclear physics and has recently been used there [37] after picking up improvements through its use in quantum chemistry. So, somewhat speculatively, we may ask whether the truncated schemes considered here could also be adapted to efficiently solve the many-body Schrodinger equation in nuclear physics, or if not such a large number of FCI states will be negligible, perhaps due to the three-body interaction between nucleons.

We have presented our recent results to show how non-variational properties (multipole moments) may also be satisfactorily calculated using one of the novel methods for truncation: Monte Carlo configuration interaction (MCCI). We demonstrated that potential curves may be computed, using only a very small fraction of the states of a full configuration interaction, to sufficient accuracy, and in a sense, more accuracy than that of its constituent single-point energies, using MCCI. In addition we have shown, for a test system, that approximate natural orbitals may be employed to accelerate a MCCI calculation. Furthermore, diffusion or projector Monte Carlo approaches to computing the full configuration interaction wavefunction have been reviewed, and seem to offer an increase in efficiency over standard diagonalization of the Hamiltonian matrix. The diagonalization of the Hamiltonian matrix could often be the rate limiting step in non-standard truncation schemes as this has to be carried out repeatedly as new configurations are added. Hence the amalgamation of techniques discussed here may offer further improvements in the future modelling of systems using configuration interaction.

## Acknowledgements

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